

Supporting information of “Self-Assembly, Structure and Pi-Conjugation at the Interface of Poly-3-Hexylthiophene and Carbon Nanotubes”

Details of the molecular dynamics simulations and computational procedures

P3HT coordinates were obtained using GaussView¹ with the TopoTools plugin in VMD². A single P3HT 20-mer consisted of 1002 atoms including 2 terminal hydrogen atoms. SWNT coordinates were obtained using the Nanotube Builder plugin in VMD² and then relaxed separately with the Tersoff potential before the simulation.

In the single P3HT chain – single SWNT runs a simulation box much bigger than the molecules in use (2000 x 2000 x 2000 Å³) was used to avoid spurious effects. The non-bonded terms for the P3HT are taken from ref. 22 in the paper and are of the Buckingham type (as in the MM3 force field), while the P3HT – SWNT interaction are of the Lennard-Jones type with the AMBER parameters taken from ref. 24. The two were combined in the LAMMPS input file using the command:

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pair_style hybrid lj/cut 12.0 buck/coul/cut 12.0
```

followed by a listing of all interactions separately. Potential-derived charges were used as in ref. 22, and re-adjusted by less than 1% to achieve charge neutrality. The relevant section of ref. 22 from which the parameters were taken is the MM3-T-PDC force field for Tetrahexylthiophene of the additional information, and Figure S-7 therein, giving a total of 8 atom types for our case.

The bonded part of the force-field was taken from ref. 22 (same section as above) neglecting angle bending terms above the quartic one, and including bond stretching, angle bending, dihedral torsions, and harmonic improper terms. “Cross” stretch-bend terms were also included. Adoption of this choice of TINKER-style potentials in

LAMMPS was performed using CLASS 2 bond and angle styles, hybrid harmonic and opls dihedral style, harmonic improper style, full atom style, and real units.

Videos of simulation runs of P3HT and SWNT

The following files are attached to the submission (PBC implies Periodic Boundary Conditions):

- **Full video of the simulation shown in Figure 1:**

15.0SWNT_20p3ht_orthogonal.mpg

- **Full video of the simulation shown in Figure 2b:**

15.0SWNT_50p3ht_orthogonal_2

- **Full video of the simulation shown in Figure 3:**

15.0_4-cnt_20_20-p3ht_300K.mpg (Without PBC)

15.0_4-cnt_20_20-p3ht_300K_PBC.mpg (With PBC)

- **Videos analogous to Figure 3, but at different concentrations** (these contribute as single points in the plot at Figure 5, for the 15 nm long SWNT case):

15.0_1-cnt_20_20-p3ht_300K_PBC.mpg

(With PBC; one 15 nm-long SWNT, approx. 16 % wt. concentration)

15.0_2-cnt_20_20-p3ht_300K_PBC.mpg

(With PBC; two 15 nm-long SWNT, approx. 28 % wt. concentration)

Preparation and experimental setup for the optical measurements

Double-walled carbon nanotubes (DWNT, Ref. 2100, Batch LDW-P90/060103) were purchased by Nanocyl *s.a.*. Carbon purity was reported 90% for DWNT. Thermogravimetric analysis (available upon request) was used to estimate the carbon content to be higher than 92%. Multi-walled carbon nanotubes (MWNT) were purchased from Aldrich (p.n. 636495, carbon content higher than 95 %, produced by CVD method). Thermogravimetric analysis estimated the carbon content to be higher than 98%.

Regioregular P3HT was purchased from Aldrich (p.n. 445703, $M_n \sim 64,000$ g/mol, head-to-tail regiospecific conformation higher than 98.5%). Initially DWNTs were suspended in chloroform (CF) or dichlorobenzene (DCB) and dispersed using ultrasonic agitation, to promote separation of the bundles. Stable dispersion was obtained after 4-6 hours of ultrasound treatment with a concentration of nanotubes of 0.1-0.15 mg/ml or lower. The dispersion lasts from a few hours to several days depending on the solvent used (typically DCB provides the best dispersion). Poly(3-hexylthiophene) was dispersed in the same solvents but in higher concentrations of 10-20mg/ml. The relative content of the two materials in the composites was achieved by controlling the volume of solution added. Indium Tin Oxide (ITO) was purchased from Kintec Company. Preliminary cleaning was performed with ethanol and with acetone in an ultrasonic bath at 60 °C for one hour³. The ITO was further cleaned by immersing the substrate in Standard Clean 1 solution (SC1)⁴ and heating the bath at 60 °C for 20 minutes.

Composite solution concentration of 20 mg/ml and spin coating speed of 1500 rpm were used to deposit 80-100 nm active layers. Post deposition annealing was performed in a controlled temperature oven at 120 °C for one hour to promote polymer chain ordering and crystallization. Preparation of MWNT-P3HT composites was performed with the same method.

UV-Vis spectra were acquired using a Cary 5000 Probe UV-Vis spectrometer on samples deposited by spin casting on ITO. Absorbance spectra were collected in the region 200-1200 nm with a speed of 600 nm/min and using dual beam transmittance configuration.

Additional optical spectra

Figure 1 shows the MWNT-P3HT absorbance spectrum showing analogous effects to DWNT-P3HT. The increase in the relative intensity of the interchain absorption peak seems to be enhanced compared to the DWNT case, perhaps due to the larger radius of the MWNT that are able to adsorb a larger number of P3HT molecules on their flatter sidewalls. We note that a similar effect in the spectra where the interchain absorption peak has enhanced intensity at higher SWNT concentration has already been recorded for

the analogous case of poly-3-octylthiophene (P3OT) - SWNT, but not discussed explicitly⁵.

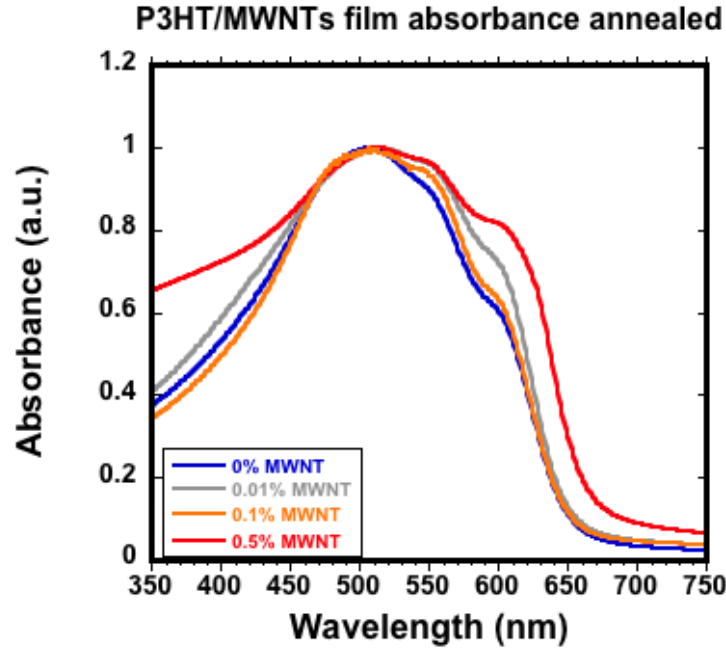


FIGURE 1. Absorption spectrum of P3HT – MWNT composites at different MWNT weight fraction. An increase in the ratio of the intensity of the peak at 620 nm to the intensity of the maximum is seen at higher MWNT concentrations and is attributed to increased conjugation order in the system, analogous to the case of P3HT-DWNT discussed in the paper.

Discussion and estimate of the impact of the conjugation length on the interface charge transfer

An estimate is provided for the impact of the conjugation length on the P3HT-SWNT charge transfer. Within a single-electron picture, and allowing for elastic electron transitions from the conduction band (CB) of the P3HT to the CB of a SWNT, we can write the transition current at finite temperature using perturbation theory as:

$$I = \frac{2\pi e}{\hbar} \sum_{L,R} f(E_R)[1 - f(E_L + \Delta\mu)] |M_{L,R}|^2 \delta(E_R - E_L)$$

where f is the Fermi distribution, e the electron charge, and $\Delta\mu$ the difference in chemical potential created by the optical excitation. L and R refer to a left and right system, which

in our case are taken to be, respectively, P3HT (the donor) and the SWNT (the acceptor). $M_{L,R}$ is the matrix element of the transition Hamiltonian between the initial electron state ψ_L in the P3HT CB and the final electron state ψ_R in the SWNT CB. In Bardeen's treatment (see ref. 38), there is no need to specify the Hamiltonian explicitly in calculating the matrix element, which can be simplified to:

$$M = \frac{\hbar^2}{2m} \int_{S_{L,R}} \psi_L \nabla \psi_R^* - \psi_R^* \nabla \psi_L dS$$

where $S_{L,R}$ is a surface placed arbitrarily between the P3HT and the SWNT where the wavefunctions and their gradients are calculated. Modeling the different conjugated parts of the polymer as chromophores contributing independently to the transition current and considering only the influence of the matrix element on the current, we write:

$$I = \sum_k I_k \propto \sum_k |M_{L,R}|^2$$

where the summation runs over the chromophores of the P3HT chain, which are separated by a large enough torsion angle ($>40^\circ$ in our case).

For each chromophore, we assume that both the P3HT and the SWNT electronic states decay exponentially in a 1-dimensional vacuum barrier along the x-direction (see Figure 2), that the P3HT wavefunction extends over a length L due to the finite polymer conjugation length along the SWNT z-direction, and for a unit length along the normal direction y.

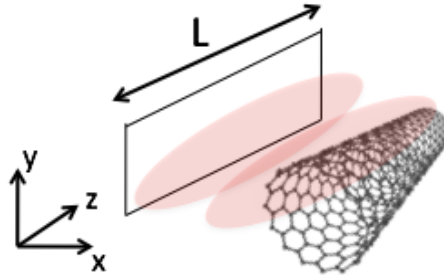


FIGURE 2. Schematic drawing of the P3HT – SWNT geometry used for the calculation. The rectangle represents a conjugated part of the P3HT of length L , and the $S_{L,R}$ surface is placed somewhere between the

two red regions, which can be thought of as the electron density of the interface electronic states. These states both decay exponentially within the barrier, and their overlap determines the strength of the transition at the particular chromophore considered.

Choosing the position of $S_{L,R}$ such that $\frac{\partial\psi_L}{\partial x} = -\frac{\partial\psi_R}{\partial x}$, and assuming that this gradient is constant throughout the surface $S_{L,R} = L$ over which the states extend, an approximate expression for the matrix element is found as:

$$M \propto \int_{S_{L,R}} \left(\psi_L \frac{\partial\psi_R}{\partial x} - \psi_R \frac{\partial\psi_L}{\partial x} \right) dS \approx 2 \cdot \psi_L \frac{\partial\psi_R}{\partial x} \cdot S_{L,R} \equiv 2L\alpha \quad (1)$$

where for the integration we further assumed $\psi_L \approx \psi_R$ at $S_{L,R}$ and used $S_{L,R} = L$ (i.e. the conjugation length), and α is $\psi_L \frac{\partial\psi_R}{\partial x}$ evaluated at the surface $S_{L,R}$ (i.e. a constant).

From (1) an estimate of the impact of the conjugation length follows immediately. For a polymer with average conjugation length L , the contribution of a single chromophore to the current is $I_k \propto |2\alpha L|^2 = 4\alpha^2 L^2$. Taking two P3HT chains of equal length but different conjugation lengths, one with larger conjugation length $L_>$ and the other with shorter conjugation length $L_<$, the ratio of the transition currents for the two chains will clearly be given by

$$\frac{I_>}{I_<} \approx \frac{L_>}{L_<} \quad (2)$$

($I_>$ and $I_<$ are the currents for the chain with greater conjugation and smaller conjugation, respectively) since the ratio of the current from the chromophores is $\left(\frac{L_>}{L_<}\right)^2$ but there will be chromophores in excess by a factor of $\frac{L_>}{L_<}$ in the chain with shorter conjugation length.

Geometrical factors could also be considered in the treatment, but the conclusion is still that the ratio (2) is of order $O\left(\frac{L_>}{L_<}\right)$.

This derivation supports our statement in the paper that a doubling of the conjugation length could bring about an increase of a factor between 2-20 of the charge transfer. Although clearly approximate in nature, such analysis is meant to provide only a rough, order-of-magnitude estimate of the effect. More accurate calculations of the impact of conjugation on charge transfer would need to take into account additional physical effects, such as excitonic effects. Though an increase of the conjugation length would lead to a decrease of the exciton binding energy and would therefore favor the charge transfer, it is difficult to estimate how much the binding energy of the excitons (of order 0.5-1.0 eV in SWNT, and somewhat smaller in P3HT) contribute to the poor functioning of current P3HT-SWNT devices.

REFERENCES

(1) http://www.gaussian.com/g_tech/gv5ref.htm

(2) <http://www.ks.uiuc.edu/Research/vmd/>

(3) Ma, W.; et al *Advanced Functional Materials* **2005**, 15, 1617-1622.

(4) SC1 solution corresponds to a solution 1:1:5 of $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$. H_2O_2 solution concentration was 30% volume. Ammonia solution of NH_4OH and NH_3 concentration was 28% volume.

(5) Kymakis E.; Alexandou, I.; Amaratunga, G. A. J. *Synth. Met.* **2002**, 127, 59-62. See the spectrum at Fig. 2 therein, and notice the enhancement of the peak at approx. 2.0 eV photon energy.